REACTIVE MAGNESIUM OXIDE PRODUCTS: CARBON NEUTRAL CEMENT FOR THE FUTURE?

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SUMMARY

With the large carbon dioxide emission in the Portland cement industry, the need to mitigate the emission and the intention to achieve carbon storage lead the development of alternatives to the conventional Portland cement. Among them, magnesia-based cement has gained lots of interests over the past decades. This paper presents a reactive magnesium oxide product which has comparable strength to Portland cement. The energy consumption for the production magnesia is less required than PC and it has a potential to absorb the CO_2 in the air to achieve strength development, which make it a promising carbon neutral cement.

INTRODUCTION

Now that we all reached an agreement that the climate change is one of the biggest challenges, and this was attributed to the emission of the greenhouse gas—CO_2. It was reported that the single cement industry accounted for 5% of the total carbon emission around the globe(Metz 2007). Since concrete is the second consumed item, just after water, it would cause significant reduction to the carbon emission if we are using more environmental friendly materials in the concrete.

Among the pursuits for mitigating the CO_2 emission, incorporating the industrial by-products, such as fly ash, slag and silica fume, is one method. Alternative binder systems were also proposed like geo-polymer cement and magnesia-based cement etc. The magnesia-based cement was selected mainly based on the following two reasons:

In the first place, the energy consumption for producing the same amount of magnesia is lower than Portland cement (PC). The temperature for sintering of limestone with clay to produce PC

is around 1450°C while the production of MgO can be processed at relative lower temperature at approximately 700~1000°C. The lower calcination temperature would lead to higher reactivity of the magnesium oxide.

Secondly, the carbonation occurs for both calcium and magnesia-based cement during their service, however, unlike calcium-based cement, the magnesia-based cement can absorb the CO_2 in the air forming stable carbonates and hydroxyl-carbonates. And the carbonation is beneficial for the strength development of magnesia-based cement.

The following table demonstrates different types of MgO-based cements which draws the most attention. Among them, the oxysalt-based cements (magnesium oxy-chloride cement and magnesium oxy-sulfate cement) are remaining limited application due to their poor water resistance. In terms of the magnesium phosphate cement (MPC), it can be used as rapid repairing material due to its quick setting and good bonding properties with old concrete and high early strength as well. Likewise, the strength of the MPC decreases significantly when soaking into water. On the other hand, the magnesium silicate hydrate (M-S-H) cement, derived from the reaction between magnesium oxide and a source of highly reactive silica, has good water resistance. Yet there is no report on the commercial application of magnesium silicate hydrate cement and limited studies on its hydration and mechanical properties, nor its long-term durability.

Table 1. Different Types of MgO-based Cement

	Magnesium Oxy-Chloride Cement	Magnesium Oxy-Sulfate Cement	Magnesium Phosphate Cement	Magnesium Silica Cement
Raw Materials	$MgO+MgCl_2$	$MgO+MgSO_4$	$MgO+NH_4H_2PO_4$/ KH_2PO_4	$MgO+SiO_2$
Reference	(Tooper and Cartz 1966)	(Beaudoin and Ramachandran 1978)	(Yang, Shi et al. 2013)	(Tran, Scott et al. 2017)

In this paper, to characterise the magnesia hydration and its strength development, a product that was simply mixed by magnesia and water was studied.

MATERIAL AND METHODS

The magnesia was supplied by Calix Ltd. Australia, and it was calcined from magnesite at the temperature around 700°C. D.I water was used to mix with the magnesia. The water to MgO ratio is fixed at 0.4 and no additives or aggregates were added. It was cast into 20*20mm cubic mould and were demould after 24hour. Four different curing conditions was proposed to compare their effects on magnesia hydration.

Table 2. Different Curing Conditions

Curing condition	**Relative Humidity (%)**	**Temperature (C)**	**CO2 concentration**
Ambient	~60	20	0.04%
In Water	In water	20	0
In CO_2	~60	20	100%
High temperature	~60	50	0.04%

The uniaxial unconfined compressive strength test was performed as per ASTM C 109-02. The particle size was analysed using the HORIBA's LA-350 laser diffraction particle size distribution analyser. The median size of the magnesium oxide used in this experiment is 10.03μm, and the particle size distribution is shown in the following figure.

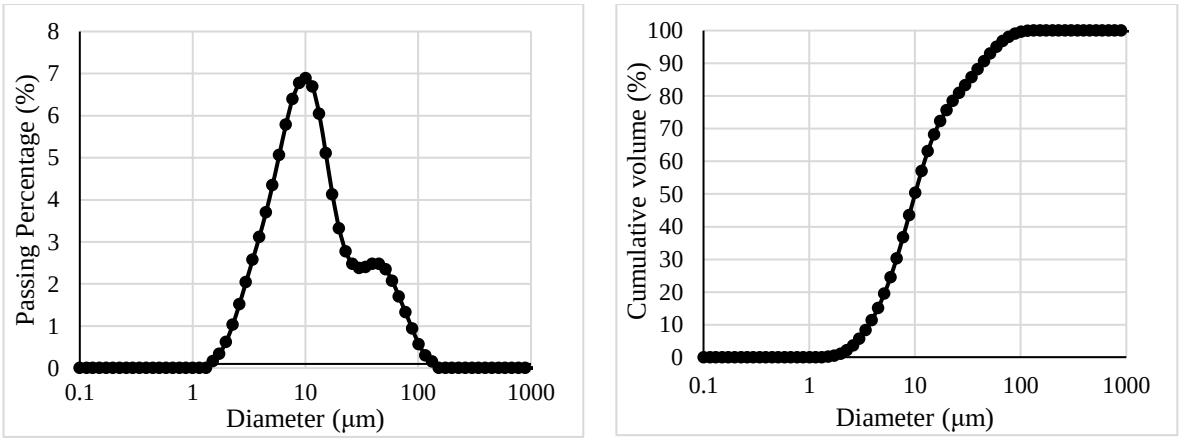

Figure 1. Particle size distribution of the MgO

In order to characterise the reaction products, thermal gravimetric analysis (TGA) and Scanning Electron Microscopy (SEM) were performed. The temperature ramp for the TGA is 20°C/min up to 1000°C and the N_2 flow rate is 100mL/min and SEM analysis was performed on a JEOL IT-300 scanning electron microscope.

RESULTS AND DISCUSSION

Characterisation of magnesia

The pH change during the mixing of 4 grams of magnesium oxide with water (80mL) was measured. The pH increased significantly once magnesia was added into the water: from 7 to 11 in the first 20 seconds.

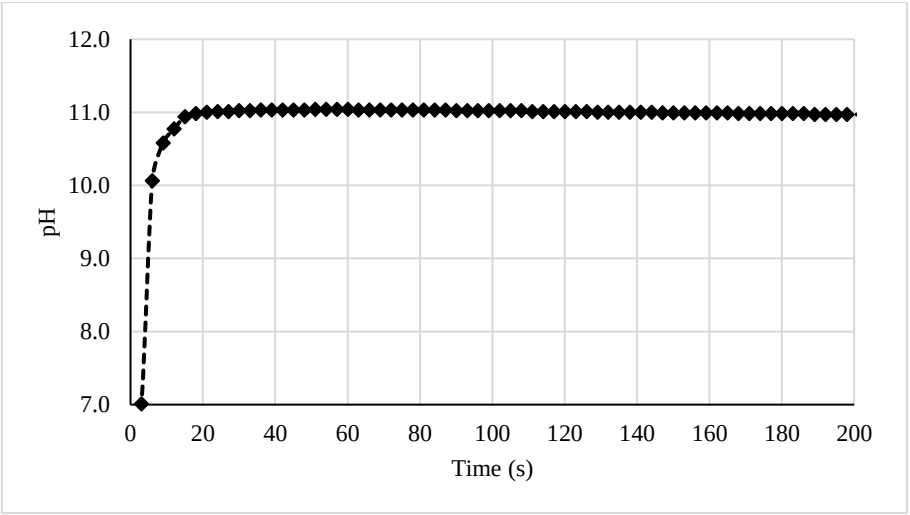

Figure 2. pH profile of MgO when mixed with water

The chemical reactivity of the MgO was measured by the acetic acidic test methods: by reacting 5.0 g of MgO with 100 mL of acetic acidic solution (1mol/L), and record the time in seconds needed for MgO to completely neutralize the acid (at pH=7) as the reactivity value. Three samples were prepared to repeat the same process and the average value is t=20s.

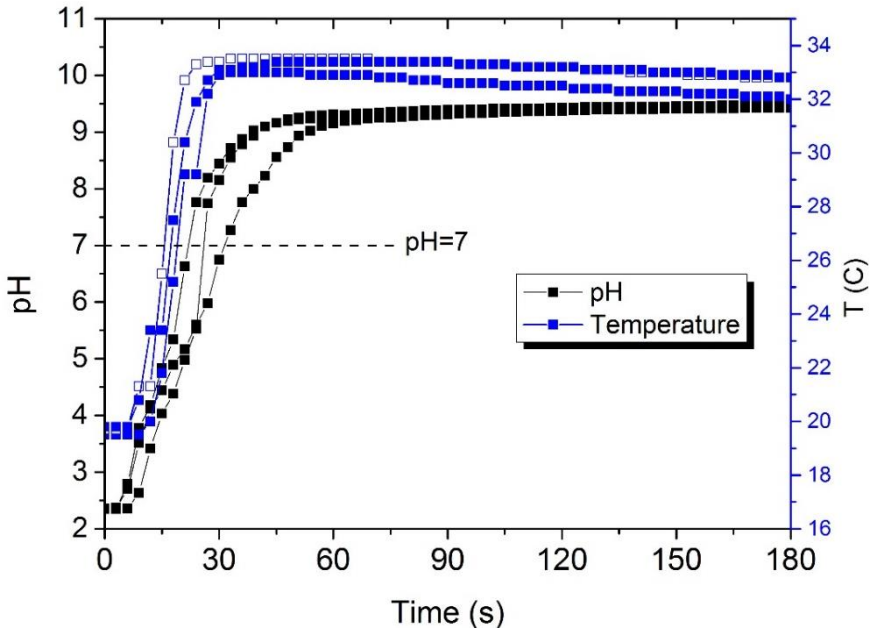

Figure 3. The chemical reactivity test of MgO

Strength development of the magnesia products

The strength development of mixture of MgO and water is shown in Fig. 4. The MgO paste cured in ambient environment performed a compressive strength of 20MPa and 25.2MPa at the age of 3 and 28 days respectively. This indicated the fast strength development in the early age while little increment occurred later.

Compared to ordinary Portland cement, curing the MgO paste in water did not have a positive influence of the strength while only 60% of the strength value of the sample cured was achieved by samples curried in air. This can be attributed to the relative quick strength development in early ages. When samples were cured with excessive water, the water plays two different roles. a). the water reacts with magnesia to form magnesium hydroxide, which is the source of the strength, on the other hand, b) the water is also dissolving the hydration products and induced the leaching of ions that led to the strength reduction.

For the samples that cured under CO2 environment, it demonstrates the same strength compared to the sample cured in ambient, however, at later age (28d), the strength reached 31MPa which is 23% higher than it counterpart. As the main hydration products from the MgO is brucite (magnesium hydroxide, $Mg(OH)_2$), it can react with the CO2 in the air with the presence of water. Due to the formation of the stable carbonates, the matrix was getting denser.

The samples cured in high temperature condition, on the contrary, showed the highest strength. The strength for the sample cured in oven for 7 days was 39.4MPa which was higher than the requirement of the general-purpose Portland cement (minimum 35MPa, at 7 days) as per NZS 3122-2009. The significant increase of strength can be attributed to the high temperature led faster reaction rate thus more hydration products were formed. However, prolong the curing time caused a strength reduction at the age of 28d, this may be attributed to the lack of free water for further hydration.

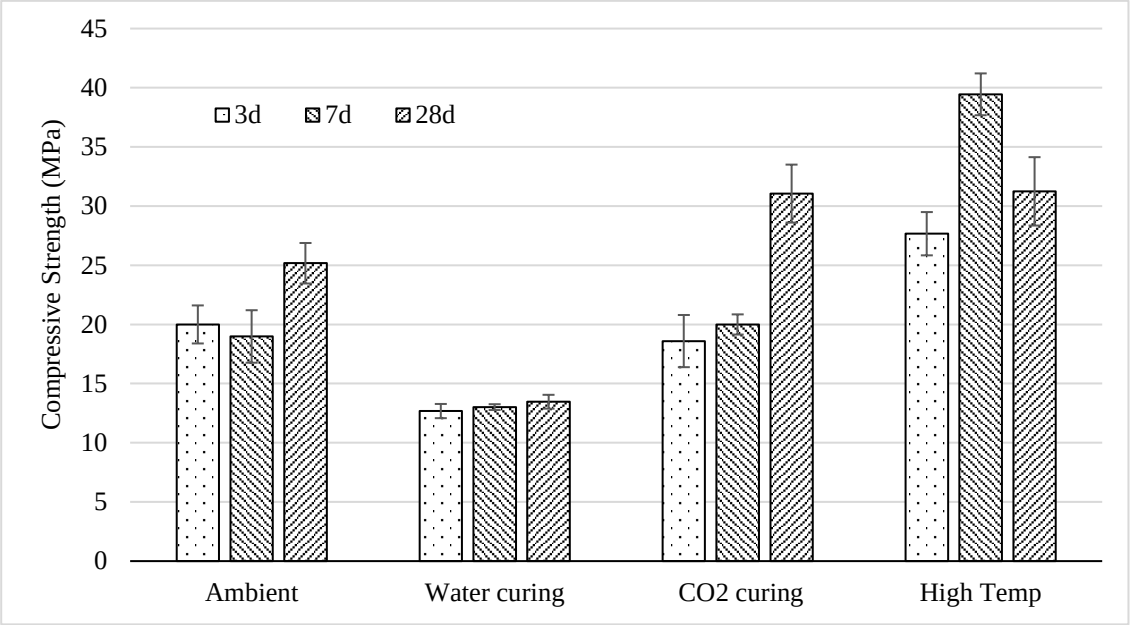

Fig.4. The strength development of MgO paste in different curing conditions

Identification of the hydration products

Figure 5 illustrate the comparison of the weight loss of MgO sample that cured in ambient environment (7d) with the pure $Mg(OH)_2$. Expect for the weight loss around 100C, which can be attributed to the evaporation of the free water, the main mass change for the MgO sample is around 400C and it was corresponded with the decomposition temperature of $Mg(OH)_2$.

According to the mass change and the decomposition equation:

$$Mg(OH)_2=MgO+H_2O \qquad (1)$$

the amount of $Mg(OH)_2$ can be calculated thus can infer the hydration degree of MgO.

$$D\% = \frac{M1 \times m2}{M2} \qquad (2)$$

Where, D% is the hydration degree of MgO;

M_1 and M_2 is the molar weight of MgO and H_2O, which is 40g/mol and 18g/mol, respectively;

m_2 is the weight loss of water during the range from 300C to 500C, and m_2=12%.

By calculating the value of D, this indicates 26.7% of the magnesia was reacted. Figure 6 shows the microscopy of the magnesia products after curing in ambient environment for 7 days. As it can be seen from the pictures that the magnesia surface were mainly covered by the hydration products. The hexagon products are brucite which is the source for the strength development.

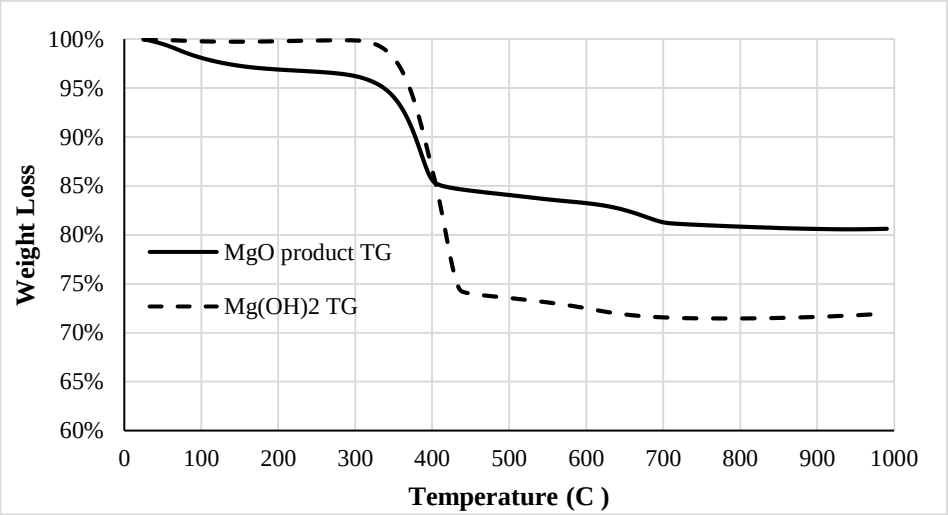

Fig.5. The thermoal gravitic analysis of the MgO products

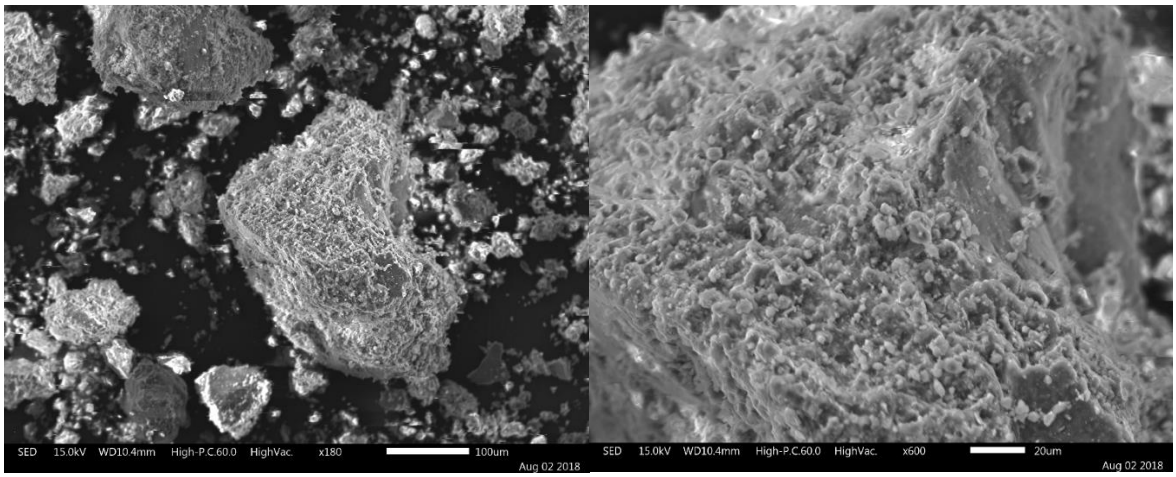

Fig.6. The microscopy of the MgO product

The reaction process of MgO

According to the above characterisation on the reaction products, we can describe the reaction process of the magnesia products. Once contacted with water, the MgO particle begins to dissolve. When it reaches the maximum solubility of its main hydration product, the magnesium hydroxide, $Mg(OH)_2$, starts to precipitate. Carbonation occurs with the presence of water and CO_2.

The following table demonstrated the proposed reaction stages.

Table 3. The reaction stages of the MgO products

Step	Stage	Reaction equation	Describe
1	Dissolution	$MgO+H_2O \rightarrow MgOH^+ + OH^-$	MgO plays an electron donator role in water
2		$MgOH^+ + OH^- \rightarrow MgOH^+ \cdot OH^-$	OH^- are adsorbed in the positively charged surface:
3		$MgOH^+ \cdot OH^- \rightarrow Mg^{2+} + 2OH^-$	OH^- anions are desorbed from the surface, releasing magnesium ions into the solution:
4	Precipitation	$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$	Ions concentration reaches the solution supersaturation, then the hydroxide starts to precipitate on the surface:
5	Carbonation	$2OH^- + H_2O + CO_2 \rightarrow CO_3^{2-} + 2\ H_2O$	If with the presence of water and carbon dioxide, the carbonation occurs.

CONCLUSION AND FUTURE STUDIES

The strength of the MgO products develops quickly in early ages, and using high temperature curing favour the early strength development. Water curing is not necessary for the MgO products and curing in CO_2 can increase its later strength. The main hydration products cured in ambient environment is brucite which was identified by TG and SEM.

In the future, more study can be done on the characterisation on the hydration mechanism and the products durability. To achieve carbon neutral or carbon storage, the effect of carbonation can be further investigated, such as comparing the hydration products in vacuum, different humidity with different CO_2 concentrations. Porous products need to be made which can have more surface area to absorb the CO_2 and building block could be one of the potential application in industry.

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